

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of : Hsu et al.
Serial No. : 09/819,237
Filing Date : March 28, 2001
For : AROMATIC POLYOL END-CAPPED UNSATURATED
POLYETHERESTER RESINS AND RESIN COMPOSITIONS
CONTAINING THE SAME HAVING IMPROVED CHEMICAL
AND/OR WATER RESISTANCE
Attorney Docket No. : CCP-3342-B

CERTIFICATION UNDER 37 CFR 1.8(a) and 1.10

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SUPPLEMENTAL PRELIMINARY AMENDMENT

Sir:

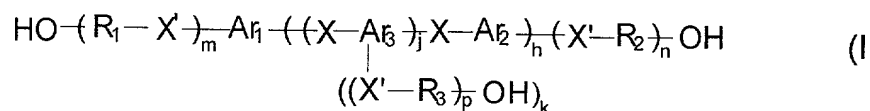
Prior to substantive examination, Applicant requests the following additional
amendments be made in the application.

IN THE CLAIMS

Please amend the claims as shown in the attached replacement sheets submitted under
37 C.F.R. § 1.12(c). The claims submitted in the Preliminary Amendment (mailed

39. A curable thermoset resin composition, comprising:

(A) at least 5 wt.% of at least one unsaturated polyetherester resin at least partially end-capped with an aromatic polyol comprising at least one non-primary hydroxy group, the aromatic polyol represented by the formula



wherein Ar₁, Ar₂ and Ar₃ each independently represents an aromatic group; R₁, R₂ and R₃ each independently represents a non-aromatic predominantly hydrocarbyl group; each X and X' independently represents a hydrocarbylene group, a hydrocarbylidene group, a divalent heteroatom or group, an ester linkage, or a combination thereof; each X' can also represent a covalent bond; h and k each independently represent an integer equal to 0 or 1; j represents an integer in the range from 0 to 5; and m, n, and p each independently represent an integer in the range from 1 to 5, provided that at least one hydroxy group of formula (I) is a nonprimary hydroxy group;

(B) at least one unsaturated polyester resin having a number average molecular weight to the average number of double bonds per polymer molecule in the range from about 200 to about 400, in an amount such that the weight ratio of polyester resin (B) to polyetherester resin (A) is in the range from about 10:90 to about 90:10;

(C) about 10 to about 70 wt.% of at least one vinyl monomer; and

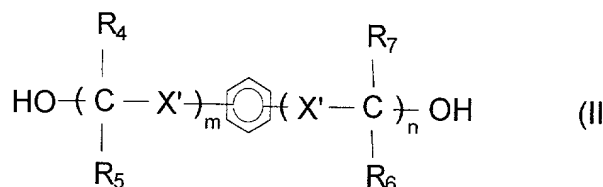
(D) at least one curing agent.

40. The composition according to Claim 39, wherein, in the aromatic polyol, Ar₁, and Ar₂ and Ar₃ when present, each represent a phenylene ring.

41. The composition according to Claim 39, wherein, in the aromatic polyol, each X, when present, represents a hydrocarbylene or hydrocarbylidene group and each X' represents a hetero atom.

42. The composition according to Claim 39, wherein, in the aromatic polyol, h is 0.

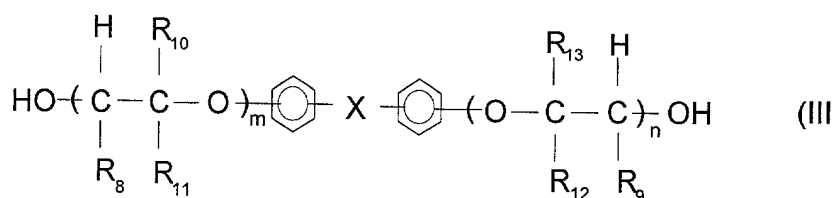
43. The composition according to Claim 42, wherein the aromatic polyol comprises at least one primary hydroxy group and is represented by the formula:



wherein R₄ to R₇ each independently represent a hydrogen atom or a hydrocarbyl group, provided that at least one hydroxy group is a nonprimary hydroxy group.

44. The composition according to Claim 39, wherein, in the aromatic polyol, h is 1.

45. The composition according to Claim 44, wherein the aromatic polyol comprises at least one primary hydroxy group and is represented by the formula:



wherein each of R_8 to R_{13} represent a hydrogen atom or a predominantly hydrocarbyl group, provided that at least one of R_8 and R_9 is not an hydrogen atom, X represents $-(CH_2)_2-$, $-S-$ or $-O-$, and m and n represent integers which individually are in the range from 1 to 5.

46. The composition according to Claim 45, wherein the aromatic polyol is a propylene oxide adduct of bisphenol A.

47. The composition according to Claim 39, wherein, in the aromatic polyol, h is 1 and j is in the range from 1 to 5.

48. The composition according to Claim 47, wherein X is a methylene, alkylene or alkylidene group.

49. The composition according to Claim 47, wherein the aromatic polyol is an alkoxylated novolac-type polymer.

50. The composition according to Claim 47, wherein the aromatic polyol is a propoxylated novolac-type polymer.

51. The composition according to Claim 39, wherein the at least one unsaturated polyetherester resin comprises the reaction product of at least one polyether and at least one ethylenically unsaturated anhydride or dicarboxylic acid wherein the anhydride or dicarboxylic acid are inserted into carbon-oxygen bonds of the polyether.

52. The composition according to Claim 51, wherein the polyether is a polyether glycol having an average hydroxyl functionality of about 2 to about 6, a hydroxyl number of about 28 to about 260 mg KOH/g, and a number average molecular weight of about 400 to about 12,000.

53. The composition according to Claim 39, wherein the unsaturated polyester resin (B) is derived from at least dicyclopentadiene, an unsaturated carboxylic anhydride, and a glycol.

54. The composition according to Claim 39, wherein the vinyl monomer (C) comprises styrene.
55. The composition according to Claims 39, wherein the curing agent (D) comprises a catalyst system comprising a free radical initiator and an accelerator.
56. The composition according to Claim 39, further comprising at least one aromatic vinyl ester resin.
57. The composition according to Claim 56, wherein the at least one aromatic vinyl ester comprises a reaction product of epichlorohydrin and bisphenol A, which is further reacted with a vinyl acid.
58. The composition according to Claim 56, wherein the at least one aromatic vinyl ester comprises the reaction product of epichlorohydrin with a novolac-type resin, which is further reacted with a vinyl acid.
59. The composition according to Claim 39, further comprising a second unsaturated polyetherester resin other than the unsaturated polyetherester resin (A).
60. The composition according to Claim 59, wherein the second unsaturated polyetherester resin comprises an unsaturated polyester resin end-capped with at least one end-capping compound selected from the group consisting of dicyclopentadiene, an epoxy-containing compound, and combinations thereof.
61. An intermediate in the form of a sheet for making a skin laminate, the intermediate comprising reinforcing fibers and the curable thermoset resin composition of Claim 39.

62. A gel coated polymer laminate comprising at least one fiber-reinforced polymer layer, at least one gel coat layer, and at least one thermoset resin layer interposed between the at least one fiber-reinforced polymer layer and the at least one gel coat layer, wherein the at least one thermoset resin layer comprises the skin laminate intermediate of Claim 61, wherein the curable thermoset resin composition is cured.

63. The gel coated laminate of Claim 62, wherein the fiber-reinforced polymer layer comprises a reinforcing fiber and a polyester resin.

64. The gel coated laminate of Claim 62, wherein the ratio of the average thickness of the at least one fiber-reinforced polymer layer and the average thickness of the at least one thermoset resin layer is about 6:1 to about 2:1.

65. A fiber-reinforced polymer composite comprising a cured composition comprising the curable thermoset resin composition of Claim 39, and a reinforcing fiber.

66. A gel coated fiber-reinforced polymer comprising the fiber-reinforced polymer composite of Claim 65 and a gel coat.

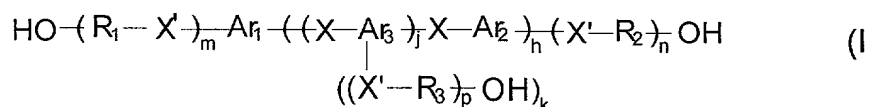
67. A gel coated polymer laminate comprising at least one fiber-reinforced polymer layer, at least one gel coat layer, and at least one thermoset resin layer interposed between the at least one fiber-reinforced polymer layer and the at least one gel coat layer, wherein the at least one thermoset resin layer comprises the curable thermoset resin composition of Claim 39.

68. The gel coated polymer laminate of Claim 67, wherein the fiber-reinforced polymer layer comprises a reinforcing fiber and a polyester resin.

69. The gel coated polymer laminate of Claim 67, wherein the ratio of the average thickness of the at least one fiber-reinforced polymer layer and the average thickness of the at least one thermoset resin layer is about 6:1 to about 2:1.

70. A curable thermoset resin composition, comprising:

(A) at least 5 wt.% of at least one unsaturated polyetherester resin at least partially end-capped with an aromatic polyol and the reaction product of at least one acid-terminated unsaturated polyetherester resin and at least one aromatic polyol having at least one non-primary hydroxy group; the at least one aromatic polyol represented by the formula:



wherein Ar₁, Ar₂ and Ar₃ each independently represents an aromatic group; R₁, R₂ and R₃ each independently represents a non-aromatic predominantly hydrocarbyl group; each X and X' independently represents a hydrocarbylene group, a hydrocarbylidene group, a divalent hetero atom or group, an ester linkage, or a combination thereof; each X' can also represent a covalent bond; h and k each independently represent an integer equal to 0 or 1; j represents an integer in the range from 0 to 5; and m, n, and p each independently represent an integer in the range from 1 to 5, provided that at least one hydroxy group of formula (I) is a nonprimary hydroxy group;

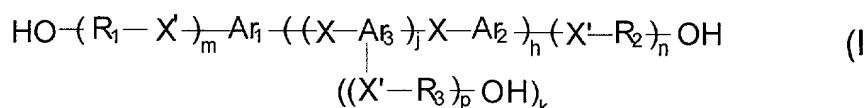
(B) at least one unsaturated polyester resin having a number average molecular weight to the average number of double bonds per polymer molecule in the range from about 200 to about 400, in an amount such that the weight ratio of polyester resin (B) to polyetherester resin (A) is in the range from about 10:90 to about 90:10;

(C) about 10 to about 70 wt.% of at least one vinyl monomer; and

(D) at least one curing agent.

71. A method for making a curable thermoset resin composition, comprising combining:

(A) at least 5 wt.% of at least one unsaturated polyetherester resin at least partially end-capped with an aromatic polyol, the aromatic polyol comprising at least one non-primary hydroxy group and represented by the formula:



wherein Ar₁, Ar₂ and Ar₃ each independently represents an aromatic group; R₁, R₂ and R₃ each independently represents a non-aromatic predominantly hydrocarbyl group; each X and X' independently represents a hydrocarbylene group, a hydrocarbylidene group, a divalent heteroatom or group, an ester linkage, or a combination thereof; each X' can also represent a covalent bond; h and k each independently represent an integer equal to 0 or 1; j represents an integer in the range from 0 to 5; and m, n, and p each independently represent an integer in the range from 1 to 5, provided that at least one hydroxy group of formula (I) is a nonprimary hydroxy group;

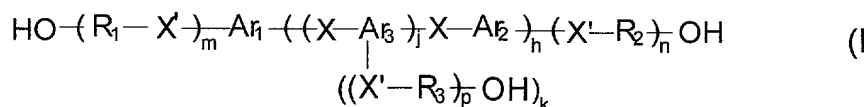
(B) at least one unsaturated polyester resin having a number average molecular weight to the average number of double bonds per polymer molecule in the range from about 200 to about 400, in an amount such that the weight ratio of polyester resin (B) to polyetherester resin (A) is in the range from about 10:90 to about 90:10;

(C) about 10 to about 70 wt.% of at least one vinyl monomer; and

(D) at least one curing agent.

72. An intermediate for making a curable thermoset resin composition comprising

(A) at least 5 wt.% of at least one unsaturated polyetherester resin at least partially end-capped with an aromatic polyol, the aromatic polyol comprising at least one non-primary hydroxy group and represented by the formula:



wherein Ar₁, Ar₂ and Ar₃ each independently represents an aromatic group; R₁, R₂ and R₃ each independently represents a non-aromatic predominantly hydrocarbyl group; each X and X'

independently represents a hydrocarbylene group, a hydrocarbylidene group, a divalent heteroatom or group, an ester linkage, or a combination thereof; each X' can also represent a covalent bond; h and k each independently represent an integer equal to 0 or 1; j represents an integer in the range from 0 to 5; and m, n, and p each independently represent an integer in the range from 1 to 5, provided that at least one hydroxy group of formula (I) is a nonprimary hydroxy group;

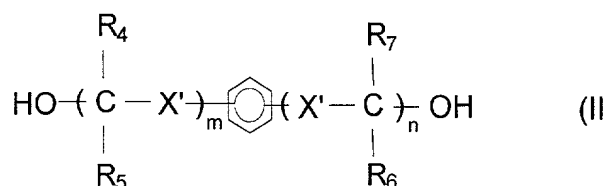
(B) at least one unsaturated polyester resin having a weight ratio of the number average molecular weight to the average number of double bonds per polymer molecule in the range from about 200 to about 400, in an amount such that the weight ratio of polyester resin (B) to polyetherester resin (A) is in the range from about 10:90 to about 90:10; and

(C) about 20 to about 50 wt.% of at least one vinyl monomer.

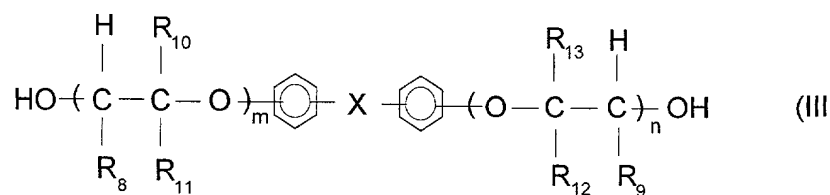
73. The intermediate according to Claim 72, further comprising a second unsaturated polyetherester resin other than the unsaturated polyetherester resin (A).

74. A curable thermoset resin composition, comprising:

(A) at least 5 wt.% of at least one unsaturated polyetherester resin at least partially end-capped with an aromatic polyol comprising at least one primary hydroxy group, the aromatic polyol represented by the formula:



wherein R₄ to R₇ each independently represent a hydrogen atom or a hydrocarbyl group, provided that at least one hydroxy group is a nonprimary hydroxy group, or



wherein each of R₈ to R₁₃ represent a hydrogen atom or a predominantly hydrocarbyl group, provided that at least one of R₈ and R₉ is not an hydrogen atom, X represents -C(CH₃)₂-, -S- or -O-, and m and n represent integers which individually are in the range from 1 to 5, or comprises an aromatic polyol prepared by alkoxyating a novolac-type polymer;

(B) at least one unsaturated polyester resin having a number average molecular weight to the average number of double bonds per polymer molecule in the range from about 200 to about 400, in an amount such that the weight ratio of polyester resin (B) to polyetherester resin (A) is in the range from about 10:90 to about 90:10;

(C) about 10 to about 70 wt.% of at least one vinyl monomer; and

(D) at least one curing agent.

75. The composition according to Claim 74, wherein the unsaturated polyester resin (B) is derived from at least dicyclopentadiene, an unsaturated carboxylic anhydride, and a glycol; the at least one vinyl monomer (C) comprises styrene; and the at least one curing agent (D) comprises a catalyst system comprising a free radical initiator and an accelerator.

76. The composition according to Claim 74, further comprising at least one aromatic vinyl ester resin.

77. An intermediate in the form of a sheet for making a skin laminate comprising reinforcing fibers and the curable thermoset resin composition according to Claim 74.

78. A fiber-reinforced polymer composite comprising a cured composition comprising the curable thermoset resin composition of Claim 74 with a reinforcing fiber.

79. A gel coated fiber-reinforced polymer comprising the fiber-reinforced polymer composite of Claim 78 and a gel coat.

80. A method for reducing blistering of a gel coated fiber-reinforced polymer comprising:
applying a curable gel coat composition to a mold;
at least partially curing the gel coat composition;
applying at least one layer of at least one curable thermoset resin composition according to Claim 39 to the at least partially cured gel coat composition;
at least partially curing the curable thermoset resin composition;
applying at least one fiber-reinforced polymer layer to the at least partially cured thermoset resin composition layer; and
curing the thermoset resin composition layer to form the gel coated fiber-reinforced polymer.

81. An article produced by the method of Claim 80.

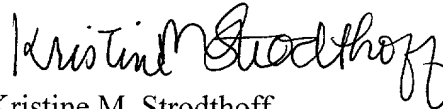
82. A method for reducing blistering of a gel coated fiber-reinforced polymer comprising:
applying a curable gel coat composition to a mold;
at least partially curing the gel coat composition;
applying at least one layer of the skin laminate intermediate of Claim 61 to the at least partially cured gel coat composition;
at least partially curing the curable thermoset resin composition; and
applying at least one fiber-reinforced polymer layer to the at least partially cured thermoset resin composition layer; and
curing the thermoset resin composition layer to form the gel coated fiber-reinforced polymer.

83. An article produced by the method of Claim 82.

March 28, 2001) were misnumbered. The claims have been properly re-numbered as Claims 39-82, and the dependencies corrected, as provided on the enclosed replacement sheets. A redline version of the claims showing the amendments is also enclosed.

It is respectfully submitted that the claims are in condition for allowance and notification to that effect is earnestly solicited. The Examiner is urged to telephone the undersigned attorney if any questions should arise.

Respectfully submitted,



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Dated: April 19, 2001

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